Preparation of N-Alkyl Acrylamides and Methacrylamides by Pyrolysis of the Corresponding Acetoxy Amides

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In a previous paper[2] it was shown that N,N-dimethylacrylamide (II) and acetic acid are obtained in high yields in the thermal decomposition of N,N-dimethyl-α-acetoxypropionamide (I). The present paper describes the preparation of certain acrylamides and methacrylamides (IV) by pyrolysis of appropriate acetoxy amides, and outlines some of the limitations of this method of making unsaturated amides.

$$\underset{\text{I}}{CH_3COOCH(CH_3)CON(CH_3)_2} \xrightarrow{520°} \underset{\text{II}}{CH_2{=}CHCON(CH_3)_2} + CH_3COOH \quad (1)$$

$$\underset{\text{III}}{CH_3COOC(CH_3)_2CONHCH_3} \longrightarrow \underset{\text{IV}}{CH_2{=}C(CH_3)CONHCH_3} + CH_3COOH \quad (2)$$

N-Methyllactamide and N-methyl-α-hydroxyisobutyramide were made conveniently by allowing methyl lactate and methyl-α-hydroxyisobutyrate, respectively, to stand with methylamine at room temperature. N,N-Diethyllactamide, N,N-dibutyllactamide, and N,N-dimethylhydroxyisobutyramide could not be prepared satisfactorily by this method because of excessively low reaction rates. Diethylamine reacted slowly with polyactic acid[3] and with the methyl ester of polyactic acid, a moderate yield of N,N-diethyllactamide being obtained.

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(2) Ratchford and Fisher, This Journal, 69, 1911 (1947).

(3) Filachione and Fisher, *Ind. Eng. Chem.*, 36, 223 (1944).

TABLE I

PROPERTIES OF N-SUBSTITUTED AMIDES

Amide	M. p., °C.	Boiling point °C.	Mm.	d^{20}_4	$n^{20}D$	$M^{20}D$ Calcd.[a]	$M^{20}D$ Obs.	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
Me lact-	71.5–72	104	1.2	.....	.....	...	...	46.8	46.6	8.9	8.8	13.6	13.6
Di-Et lact-	....	115–117	12	0.9901	1.4540	39.65	39.66	58.2	57.9[g]	..	..	9.7	9.7
Me α-hydroxyisobutyr-	72.5–73	118–120[b]	0.2	.....	.....	...	...	51.3	51.2	9.5	9.5	12.0	11.8
Me acetoxypropion-	53.5–54	116.5–117.5[b]	0.4	.....	.....	...	...	49.6	50.0	7.6	7.6	9.6	9.6[h]
Di-Et acetoxypropion-	....	76.5–78[b]	0.5	1.0212	1.4480	49.02	49.07	57.7	57.7[g]	..	..	7.5	7.4[i]
Di-Bu acetoxypropion-	....	106[b]	0.6	0.9654	1.4505	67.49	67.85	64.2	64.2	10.4	10.3	5.8	5.8
Me acetoxyisobutyr-	70–73	88–89[b]	0.4	.....	.....	...	...	52.8	52.9[g]	..	..	8.8	8.8[j]
Di-Me acetoxyisobutyr-	36.5–37.5	73.5[b]	0.2	.....	1.4520[c]	...	...	..	...	..	..	8.1	8.3
Di-Et acryl-	....	95[d]	19	0.9256	1.4672	37.66	38.06	66.1	65.9[g]	..	..	11.0	11.2
Me methacryl-	....	108–110[e]	10	0.9963	1.4700	28.69	27.76	..	...	..	..	..	...
Di-Me methacryl-	....	66–67[f]	10	0.9272[f]	1.4594[f]	33.04	33.39	..	...	..	..	12.4	12.8

[a] For the atomic refraction of N in the disubstituted compounds the value 2.49 was used (reference 16 (a)); for the monosubstituted compounds, 2.76 (D'Alelio and Reid, THIS JOURNAL, 59, 109 (1937)), and for the other atoms the values of Eisenlohr (Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1739). [b] These measurements are subject to the errors encountered in distillations in the usual laboratory equipment (Hickman, *J. Phys. Chem.*, 34, 627 (1930)). [c] For the supercooled liquid. [d] Jacobson and Mighton (U. S. Patent 2,311,548, Feb. 16, 1943) give the b. p. 93° (19 mm.). [e] Jacobson and Mighton, *ibid.*, give the b. p. 100° (10 mm.). [f] For a sample synthesized from methacrylic anhydride and dimethylamine. [g] Found by wet oxidation. [h] Sapon. equiv., calcd. 145.2, found: 144.4. [i] Sapon. equiv., calcd. 187.2, found 184.6. [j] Sapon. equiv., calcd. 159.2, found 160.5.

Probably the low reactivity of diethylamine (and the moderately high reactivities[4] of both piperidine and morpholine) toward methyl lactate can be explained on the basis of steric effects of the type discussed by Brown.[5] In a study of the addition compounds of reference acids and diethylamine,[5] Brown concluded that the configuration of diethylamine limits association with a highly hindered reference acid. If the plausible assumption is made that aminolysis occurs *via* the same mechanism as ammonolysis,[6] it is possible to consider the amide ion (or amine) the base and methyl lactate the reference acid (with association occurring between the carbonyl carbon atom and the nitrogen atom), and apply the steric theory of Brown to explain the observed phenomena.

N-Methylacetoxypropionamide, N-methylacetoxyisobutyramide (III) and N,N-diethylacetoxypropionamide were prepared by treatment of the corresponding lactamide or hydroxyisobutyramide with acetic anhydride. N,N-Diethylacetoxypropionamide, N,N-dibutylacetoxypropionamide and N,N-dimethylacetoxyisobutyramide (Table I) were made by the reaction of the proper dialkylamine with α-acetoxypropionyl chloride or α-acetoxyisobutyryl chloride.

The lower acetoxy amides of the present work were similar to N,N-dimethylacetoxypropionamide,[2] in that the amide, but not the acetoxy groups, were resistant to saponification (Table I).

N,N-Diethylacrylamide and acetic acid were the principal products of the thermal decomposition (500 to 550°) of N,N-diethylacetoxypropionamide, and therefore the pyrolysis method is suitable for the preparation of both N,N-dimethyl- and N,N-diethylacrylamide. A brief study of the pyrolysis of N-methyl- and N,N-dibutylacetoxypropionamide, however, indicated that the pyrolysis of α-acetoxy-propionamides is less satisfactory for producing N-monoalkylacrylamides or the higher N,N-dialkylacrylamides.

As pointed out earlier,[2] the pyrolysis behavior of N,N-dimethylacetoxypropionamide resembles that of its oxygen analog, methyl acetoxypropionate, in that acetic acid and an acrylic acid derivative are the principal products. The thermal decomposition of the N,N-diethyl amide, however, was distinctly different from that of ethyl acetoxypropionate, which yielded ethylene instead of ethyl acrylate as a major decomposition product.[7]

The pyrolysis behavior of N-methylacetoxypropionamide was similar to that of alkyl lactates[8] and α-acetoxypropionic acid[8] in that acrylic acid or its derivatives were formed in low yield. The common feature of alkyl lactates, acetoxypropionic acid, and N-methylacetoxypropionamide is the presence of hydrogen attached to oxygen or nitrogen, and therefore it appears that lactic acid derivatives having an O- or N-hydrogen (and perhaps S-hydrogen) are unsuitable for pyrolytic conversion into the corresponding acrylic acid derivatives.

It has been postulated[9] that the normal thermal decomposition of acetates (equation 3, X = H or alkyl) involves the transient formation and subsequent decomposition of a ring such as V into an olefinic product (VI) and acetic acid. When the acetate (or other ester) contains —COOH or —CONHR as substituents (that is, X = carboxyl or amide groups), the formation of rings[10] such

(4) Ratchford and Fisher, "Preparation of N-Substituted Lactamides," presented before the Division of Organic Chemistry at the 112th Meeting of the American Chemical Society, New York, N. Y., September 18, 1947.

(5) Brown and Taylor, THIS JOURNAL, 69, 1332 (1947); Spitzer and Pitzer, *ibid.*, 70, 1261 (1948).

(6) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 359; Gordon, Miller and Day, THIS JOURNAL, 70, 1946 (1948).

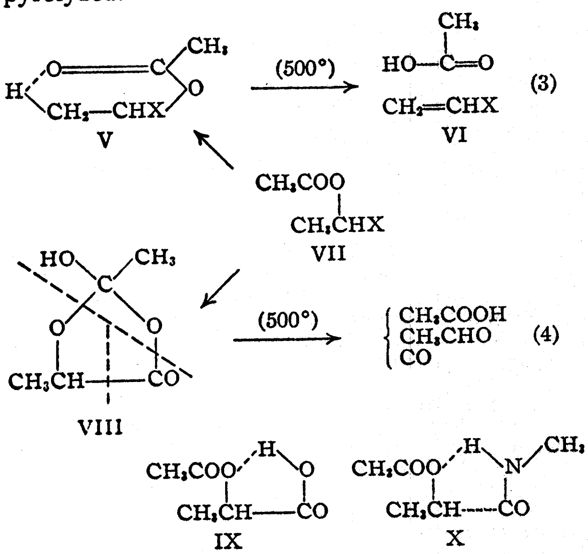
(7) Burns, Jones and Ritchie, *J. Chem. Soc.*, 400, 1054 (1935); Rehberg and Fisher, THIS JOURNAL, 67, 56 (1945).

(8) Hurd, "Pyrolysis of Carbon Compounds," ACS Monograph 50, Reinhold Publishing Corp., New York, N. Y., 1929, pp. 426, 535.

(9) Hurd and Blunck, THIS JOURNAL, 60, 2419 (1938).

(10) Somewhat similar rings have been proposed as the intermediates in several reactions (Arnold, "Stereochemistry of Five- and Six-membered Rings," presented before the Tenth National Organic Chemistry Symposium, American Chemical Society, Boston, Mass., June 12–14, 1947).

as VIII, IX, or X might take preference over that of the usual or normal intermediate (V). Scission of the bonds as shown in equation 4 might be responsible for decomposition into acetic acid, acetaldehyde and carbon monoxide, the products actually formed when α-acetoxypropionic acid is pyrolyzed.[8]



Both N-methyl-(IV) and N,N-dimethylmethacrylamide were obtained satisfactorily by pyrolyzing the corresponding α-acetoxyisobutyramides. These results suggest that α-acetoxyisobutyramides generally decompose more readily than α-acetoxypropionamides into the corresponding unsaturated amides. It has been demonstrated[11] that α-acetoxyisobutyrates decompose more readily than the corresponding α-acetoxypropionates into methacrylic or acrylic esters.

The success of the pyrolytic method for preparing these acrylamides and methacrylamides suggests that it may be useful in preparing certain crotonamides and amides of other unsaturated acids.

The pyrolysis of alkyl acetoxypropionates, which contain two ester groups, affords a comparison of the thermal stability of esters of acetic and α-acetoxypropionic acids.[7] Since N,N-diethylacetoxypropionamide contains both ester and amide groups, results obtained by pyrolyzing this compound may be used as a measure of the relative thermal stability of ester and amide groups; the formation of the acrylamide as the principal product indicates that the amide group is more stable.

Acknowledgment.—The authors gratefully acknowledge the assistance of C. O. Willits, Ruth W. Brand, Betty B. Linker and Pauline McDowell, who supplied most of the analytical data, and the interest and helpful suggestions of Allan R. Day.

(11) Filachione, Lengel and Fisher, THIS JOURNAL, **68**, 330 (1946).

Experimental

N,N-Diethyllactamide (Table I).—When it was found that this lactamide was not obtained by the usual preparative method for lactamides,[2] other methods were tried. In the most successful experiment, 2 equivalents of polylactic acid (equiv. wt. 79) and excess diethylamine were circulated counter-currently through a heated tower[12] maintained at 175° and packed with 1/4-inch porcelain Berl saddles for five six-hour periods (1 pass per period). At the end of each period, the product from the tower was distilled to recover N,N-diethyllactamide; all other fractions, including the residue, were returned to the tower, and the process was repeated. At the end of successive periods, the total conversions to diethyllactamide were 18, 38, 53, 61 and finally 72%.

N-Methyllactamide (Table I) was obtained in 91% yield by distilling a mixture of 2 moles of methyl lactate, 2 moles of methylamine and 0.2 ml. of concentrated sulfuric acid that had been stored at room temperature for three weeks. The catalyst was neutralized with sodium acetate before distillation.

N-Methyl-α-hydroxyisobutyramide was obtained in 97% yield by distilling a mixture of 2 moles methyl hydroxyisobutyrate, 2 moles methylamine and 0.2 ml. concentrated sulfuric acid that had been stored at room temperature for two months (catalyst neutralized before distillation).

Acetylation of N-Alkyllactamides.—N-Methyllactamide and N,N-diethyllactamide were acetylated with acetic anhydride by the method used previously with N,N-dimethyllactamide,[3] high yields (98 and 95%) of the corresponding α-acetoxypropionamides being obtained.

Reaction of α-Acetoxypropionyl Chloride with Amines.—Acetoxypropionyl chloride (2.2 moles) was allowed to react with 2 moles of diethylamine. N,N-Diethyl-α-acetoxypropionamide was obtained in 66% yield by distillation of the reaction mixture. N,N-Dibutyl-α-acetoxypropionamide (69% yield) and N,N-dimethyl-α-acetoxyisobutyramide (78% yield) were made similarly from the appropriate acid chlorides and amines.

N-Methyl-α-acetoxyisobutyramide was prepared in 50% yield from N-methylhydroxyisobutyramide and 10% excess acetic anhydride, concentrated sulfuric acid being used as catalyst. After the catalyst had been neutralized and the acetic acid distilled, the acetoxy amide was collected at 118° (0.3 mm.). The low yield was due to the formation of viscous tacky fractions.

In determining the saponification equivalents[13] of Table I, a weighed sample was dissolved in 25 ml. of neutral ethanol cooled in ice-water, and titrated to determine free acidity, if any. Then 25 ml. of 0.2 N sodium hydroxide in ethanol was added. The weight of the sample was taken so that the alkali would be present in 50% excess of the ester group. The solution was refluxed on a steam-bath for one hour (air condenser), 50 ml. of distilled water was added, and refluxing was continued for another hour. At this point the condenser was rinsed, and excess alkali was back-titrated with 0.1 N hydrochloric acid, cresol red–thymol blue mixed indicator being used.

Pyrolysis Experiments.—Essentially the equipment and method described previously[14] were used. In some instances the acetoxy amide was dissolved in benzene prior to pyrolysis. The pyrolyzates were distilled (after a small amount of hydroquinone was added to prevent polymerization) to determine the nature and amounts of the products.

A solution consisting of 185.5 g. of N-methylacetoxypropionamide and 138.5 g. of benzene was pyrolyzed at 524° at a rate of 0.6 mole per hour of the amide (contact time, 2.9 sec., for the tube within 15° of 524°). The recovery of liquid products (1 g. of which neutralized 3.59 ml. N NaOH) was 97.2%. The following products were obtained on distillation (yields are expressed as per cent. of moles of acetoxy amide pyrolyzed): acetic acid, 87%,

(12) Filachione, Lengel and Fisher, *Ind. Eng. Chem.*, **37**, 388 (1945).

(13) We are indebted to C. O. Willits and his associates for his method and the saponification equivalents.

(14) Fein, Ratchford and Fisher, THIS JOURNAL, **66**, 1201 (1944).

Table II

Pyrolysis of N-Alkyl Acetoxy Amides

Expt.	Amide pyrolyzed	G.	Temp., °C.	Contact time, sec.	Pyrolysis rate, mole/hr.	Liquid pyrolyzate %	Liquid pyrolyzate N NaOH to neutralize 1 g., ml.	Acetoxy amide recovered, %	Yield, % Alkyl acryl amide	Yield, % Acetic acid Titration	Yield, % Acetic acid Distillation
1	Di-Et-acetoxypropionamide	110	506	2.5	0.452	96	3.16	28	77[a]	79	40
2	Di-Et-acetoxypropionamide	169.5	520	1.7	.548	97	4.69	17	75[a]	86	77
3	Di-Et-acetoxypropionamide	255	523	4.5	.296	96	4.83	0	66[b]	87	56
4	Di-Et-acetoxypropionamide	257	520	1.6	.55	98.5	3.95	16	72[a]	87	78
5	Di-*n*-Bu-acetoxypropionamide	49	507	2.7	.546	100	2.10	[c]	31[d]	50	34
6	Me-acetoxyisobutyramide	95[e]	476	1.2	.842	100	2.12	9	65	76	64
7	Di-Me-acetoxyisobutyramide	71[f]	480	1.7	.877	99	2.62	0	87[a]	95	59

[a] Corrected for acidic material, principally acetic acid, present. [b] Acid-free material. [c] Not definitely identified. [d] Crude, but polymerizable, material. [e] A solution of 95 g. of amide and 81 g. of benzene was pyrolyzed. [f] A solution of 71 g. of amide and 81 g. of benzene was pyrolyzed.

and water, 30–44%. A fraction of impure N-methylacrylamide was obtained (approximately 30% yield). The contents of the trap (cooled with solid carbon dioxide) had an aldehyde odor; treatment with 2,4-dinitrophenylhydrazine gave a compound identified as the acetaldehyde derivative: m.p., 165.5–166, mixed m. p., 165°.

Anal. Calcd. for $C_8H_8O_4N_4$: N, 25.0; C, 42.9; H, 3.6. Found: N, 24.6; C, 42.9; H, 3.8. The results of other pyrolysis experiments are given in Table II.

When the pyrolyzates of N,N-diethylacetoxypropionamide were distilled, it was found that the acrylamide fractions contained acetic acid (compare yields of acetic acid in Table II found by titration and distillation). In experiment 3 the crude acrylamide fractions were treated with aqueous sodium carbonate and extracted with ether. The ether extract was distilled, yielding an acid-free distillate having physical constants identical with those of the acrylamide made from acrylyl chloride and diethylamine. In experiment 4 the crude acrylamide fractions (containing 6% acetic acid) were redistilled, yielding the acrylamide containing 2.4% acid. In experiment 2 the crude diethylacrylamide fractions (with 7% acid) were redistilled to give the acrylamide with 0.9% acid; the yield of this material was 54% (based on acetoxy amide destroyed). In this experiment analysis of the gaseous products showed yields of 12, 5 and 2% for carbon monoxide, unsaturates and saturates, respectively.

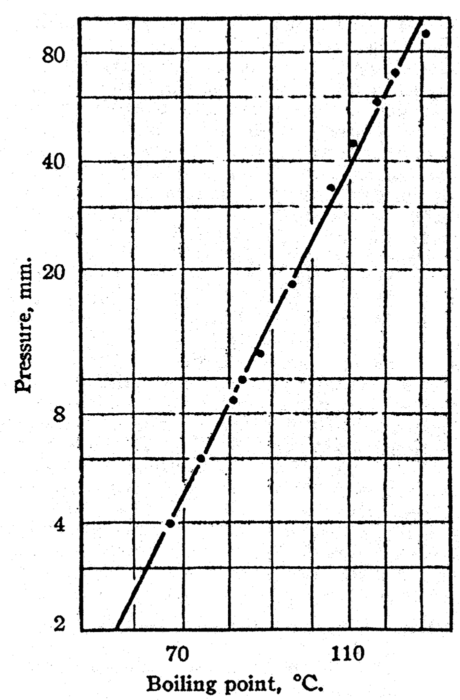


Fig. 1.—Boiling points of N,N-diethyl acrylamide.

Figure 1 shows a boiling point curve for N,N-diethylacrylamide.

When the pyrolyzate of N,N-dimethylacetoxyisobutyramide was distilled, 96% of all the acid charged was recovered in the distillate fractions; of the acid distilled, 24% was collected in the "N,N-dimethylmethacrylamide fractions." The latter distilled at 69–71° (10 mm.), but the acid content ranged from 18 to 6%, and $n^{20}D$ from 1.4481 to 1.4558. The acid content of the combined fractions was 13%. When heptane (in excess of that required for the reported heptane–acetic acid azeotrope[15]) was added to the combined fractions and the mixture carefully distilled, 96% of the acid charged was recovered; of this, 67% appeared in the "methacrylamide fractions," which distilled at 70° (10 mm.). The individual fractions showed acid contents from 15.6 to 5.2%; $n^{20}D$ ranged from 1.4498 to 1.4568.

Thus N,N-dimethylmethacrylamide strongly resembles N,N-dimethacrylamide in distilling with acetic acid.[2] Other N,N-disubstituted amides have been reported to form maximum boiling azeotropes with acetic acid.[16] The relatively large affinity of the N,N-dialkyl amides for acetic acid might be due to the increased electron density around the nitrogen caused by the presence of two electron-releasing alkyl groups. Possibly steric factors[6] are responsible for the fact that the N,N-diethyl amides have less attraction for acetic acid than the N,N-dimethyl amides. The N-methylacrylamide and N-methylmethacrylamide fractions were essentially acid-free.

Polymeric Acrylamides.—N,N-diethylacrylamide was polymerized in mass and in water solution, benzoyl peroxide and ammonium persulfate, respectively, being used as initiators.

Polymeric N,N-diethylacrylamide was moderately hard and transparent. It resembled polymeric N,N-dimethylacrylamide in appearance, but was much different in solubility characteristics. The polymeric N,N-diethylamide dissolved readily in benzene, toluene and acetone, and swelled in water, chloroform and carbon tetrachloride. A polymer prepared by polymerizing an aqueous solution of N,N-diethylacrylamide was more soluble in cold water than in hot water. It precipitated from hot water as a soft tacky mass.

A sample of impure N-methylacrylamide on storage in a refrigerator at about 5° darkened and polymerized slowly to a viscous tacky mass that was soluble in water but insoluble in chloroform, benzene, toluene, carbon tetrachloride, acetone, ethyl acetate and heptane.

(15) L. H. Horsley, *Anal. Chem.*, **19**, 508 (1947).

(16) (a) Ruhoff and Reid, This Journal, **59**, 401 (1937); (b) Hanford and Stevenson, U. S. Patent 2,231,905 (Feb. 18, 1941).

Summary

The pyrolysis method used previously to transform the acetyl derivatives of N,N-dimethyllactamide into N,N-dimethylacrylamide was applied to the preparation of other N-alkyl acrylamides and methacrylamides. N,N-Diethylacrylamide was obtained in good yield by the thermal decomposition of N,N-diethyl-α-acetoxypropionamide, but pyrolysis of N-methyl- and N,N-di-n-butyl-acetoxypropionamide was less satisfactory for the preparation of the corresponding acrylamides.

N-Methyl- and N,N-dimethylmethacrylamides were made successfully by pyrolyzing the corresponding N-alkyl α-acetoxyisobutyramides. Apparently methacrylamides can be made more readily than acrylamides by the pyrolysis method.

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